| | | | | |
|---|---|---|---|---|
| H6 | 0.330 (4) | 0.029 (3) | 0.125 (2) | 0.040 (7) |
| H7 | 0.954 (4) | −0.050 (2) | 0.344 (2) | 0.025 (6) |
| H8 | 1.111 (4) | 0.075 (2) | 0.406 (2) | 0.027 (6) |
| H9† | 0.474 (8) | 0.498 (5) | 0.050 (4) | 0.03 (1) |
| H10 | 0.299 (4) | 0.509 (3) | 0.120 (2) | 0.048 (8) |
| H11† | 0.47 (1) | 0.595 (6) | 0.156 (5) | 0.06 (2) |

† Occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Cl1—O1 | 1.430 (1) | N1—C2 | 1.341 (2) |
| Cl1—O2 | 1.433 (1) | N2—C2 | 1.347 (2) |
| Cl1—O3 | 1.436 (1) | N2—C3 | 1.378 (2) |
| Cl1—O4 | 1.458 (1) | N3—C1 | 1.333 (2) |
| Cl2—O5 | 1.449 (1) | N3—C3 | 1.320 (2) |
| Cl2—O6 | 1.430 (1) | N4—C1 | 1.301 (2) |
| Cl2—O7 | 1.437 (1) | N5—C2 | 1.304 (2) |
| Cl2—O8 | 1.441 (1) | N6—C3 | 1.309 (2) |
| N1—C1 | 1.376 (2) | | |
| | | | |
| O1—Cl1—O2 | 109.89 (8) | C1—N1—C2 | 120.3 (1) |
| O1—Cl1—O3 | 110.11 (7) | C2—N2—C3 | 120.2 (1) |
| O1—Cl1—O4 | 108.85 (8) | C1—N3—C3 | 117.2 (1) |
| O2—Cl1—O3 | 110.19 (8) | N1—C1—N3 | 122.1 (1) |
| O2—Cl1—O4 | 109.00 (7) | N1—C1—N4 | 118.4 (2) |
| O3—Cl1—O4 | 108.78 (7) | N3—C1—N4 | 119.5 (1) |
| O5—Cl2—O6 | 109.36 (8) | N1—C2—N2 | 117.9 (1) |
| O5—Cl2—O7 | 108.77 (9) | N1—C2—N5 | 121.7 (2) |
| O5—Cl2—O8 | 108.7 (1) | N2—C2—N5 | 120.4 (2) |
| O6—Cl2—O7 | 110.86 (8) | N2—C3—N3 | 122.2 (2) |
| O6—Cl2—O8 | 109.64 (9) | N2—C3—N6 | 117.4 (1) |
| O7—Cl2—O8 | 109.43 (8) | N3—C3—N6 | 120.4 (1) |

Table 3. *Hydrogen-bonding geometry* (Å, °)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···O9 | 0.84 (3) | 1.88 (3) | 2.705 (2) | 170 (2) |
| N2—H2···O4$^{i}$ | 0.85 (2) | 2.30 (2) | 3.021 (2) | 142 (2) |
| N2—H2···O7$^{ii}$ | 0.85 (2) | 2.48 (2) | 2.931 (2) | 114 (2) |
| N4—H3···O3$^{ii}$ | 0.83 (2) | 2.18 (2) | 2.982 (2) | 162 (2) |
| N4—H4···O4 | 0.80 (2) | 2.26 (2) | 3.033 (2) | 161 (2) |
| N5—H5···O5$^{iii}$ | 0.78 (2) | 2.11 (2) | 2.854 (2) | 159 (2) |
| N5—H6···O8 | 0.94 (2) | 1.95 (2) | 2.884 (2) | 173 (2) |
| N6—H7···O1$^{iv}$ | 0.86 (2) | 2.40 (2) | 2.804 (2) | 110 (2) |
| N6—H7···O4$^{i}$ | 0.86 (2) | 2.25 (2) | 2.983 (2) | 143 (2) |
| N6—H8···O2$^{v}$ | 0.81 (2) | 2.16 (2) | 2.951 (2) | 168 (2) |
| O9—H9···O9$^{vi}$ | 0.85 (4) | 2.01 (4) | 2.860 (2) | 176 (5) |
| O9—H10···O6$^{vii}$ | 0.76 (3) | 2.30 (3) | 2.998 (2) | 153 (3) |
| O9—H11···O4 | 0.88 (5) | 2.34 (5) | 3.146 (2) | 152 (5) |

Symmetry codes: (i) $x, y-1, z$; (ii) $1+x, y, z$; (iii) $-x, -y, -z$; (iv) $1+x, y-1, z$; (v) $2-x, 1-y, 1-z$; (vi) $1-x, 1-y, -z$; (vii) $x, 1+y, z$.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The structure was solved by Patterson and Fourier methods.

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN PROCESS* (Fair, 1990) and *SORTAV* (Blessing, 1987). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *CAChe WORKSYSTEM* (Cache Scientific, 1993). Software used to prepare material for publication: *MolEN CIF VAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Blessing, R. H. (1987). *Cryst. Rev.* **1**, 3–57

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

Cache Scientific (1993). *CAChe Reference Manual*. Cache Scientific, Beaverton, Oregon, USA.

Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Wang, Y., Wei, B. & Wang, Q. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 79–84.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

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# 1,8-Dimethyl-2-(3-furoylaminomethyl)-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepin-4-ium Chloride

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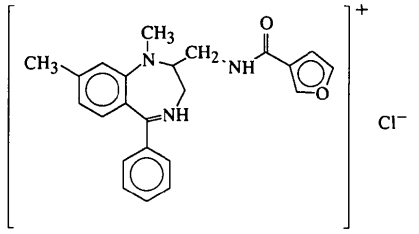
## Abstract

The diazepine ring of the title compound, $C_{23}H_{24}N_3O_2^+.Cl^-$, adopts a conformation halfway between a distorted boat and a distorted sofa. The furoylaminomethyl side chain is in an extended conformation placing the furan ring nearly parallel to the benzo part of the benzodiazepine ring. Two intramolecular hydrogen bonds to the $Cl^-$ anion stabilize the observed conformation.

## Comment

As part of a structure–activity study on a series of 2-acylaminomethylbenzodiazepine derivatives with opioid activity, the crystal structure of the title compound, (I), has been determined.

Compared to the five other structures of the series determined previously (Peeters, Blaton, Meurisse & De Ranter, 1994*a*,*b*, and references cited therein), the title structure does not show any unexpected features. The seven-membered ring is in the usual conformation halfway between a distorted boat and a distorted sofa




(I)

[puckering parameters $q_2 = 0.684\,(4)$, $q_3 = 0.289\,(3)$ Å, $\varphi_2 = -36.2\,(3)$, $\varphi_3 = -135.9\,(7)°$] with the 2-substituent axial and a mirror plane through C3 and the centre of the C5a—C9a bond [asymmetry parameter $\Delta C_s$(C3) = 0.063 (1)]. The furan ring is nearly parallel to the benzo part of the diazepine ring [dihedral angle 10.4 (1)°], which in turn forms a dihedral angle of 62.7 (1)° with the phenyl ring. The conformation of the benzamide side chain is stabilized by two intramolecular hydrogen bonds, one from N4 and one from N12 to the $Cl^-$ anion [N4—H4 = 0.860, N4···Cl = 3.056 (3), H4···Cl = 2.26 Å, N4—H4···Cl = 153.1°; N12—H12 = 0.860, N12···Cl = 3.222 (3), H12···Cl = 2.40 Å, N12—H12···Cl = 159.0°].

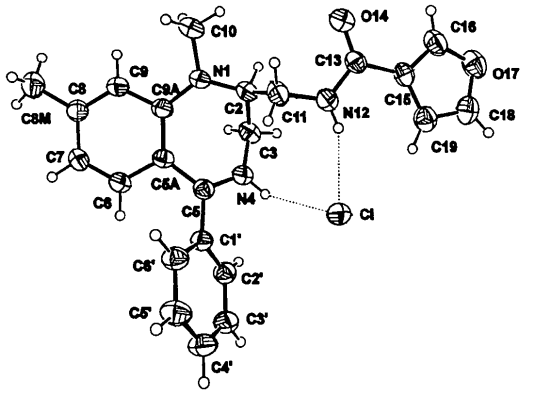



Fig. 1. Perspective view of the title compound with atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

## Experimental

The title compound was provided by Kali-Chemie, Pharma GmbH, Hannover, Germany, and recrystallized from an amylacetate/ethanol solution. The density $D_m$ was measured by flotation in *n*-heptane/$CCl_4$.

*Crystal data*

| | |
|---|---|
| $C_{23}H_{24}N_3O_2^+.Cl^-$ | Cu $K\alpha$ radiation |
| $M_r = 409.90$ | $\lambda = 1.54184$ Å |
| Orthorhombic | Cell parameters from 24 reflections |
| $Pbc2_1$ | $\theta = 20$–$21°$ |
| $a = 7.653\,(4)$ Å | $\mu = 1.760$ mm$^{-1}$ |
| $b = 15.98\,(1)$ Å | $T = 293$ K |
| $c = 17.57\,(1)$ Å | Prism |
| $V = 2150.\,(2)$ Å$^3$ | 0.60 × 0.40 × 0.15 mm |
| $Z = 4$ | Orange |
| $D_x = 1.267$ Mg m$^{-3}$ | |
| $D_m = 1.269$ Mg m$^{-3}$ | |

*Data collection*

| | |
|---|---|
| Stoe Stadi-4 four-circle diffractometer | 1564 observed reflections [$F^2 > 2\sigma(F^2)$] |
| $\theta/\omega$ scans | $R_{int} = 0.0262$ |
| Absorption correction: | $\theta_{max} = 59.23°$ |
| $\psi$ scans (*EMPIR*; Stoe & Cie, 1992*a*) | $h = -8 \rightarrow 8$ |
| $T_{min} = 0.362$, $T_{max} = 0.482$ | $k = 0 \rightarrow 17$ |
| 3382 measured reflections | $l = 0 \rightarrow 19$ |
| 1621 independent reflections | 3 standard reflections |
| | frequency: 60 min |
| | intensity decay: < 3.0% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Extinction correction: *SHELXL*93 (Sheldrick, 1993) |
| $R[F^2 > 2\sigma(F^2)] = 0.0334$ | Extinction coefficient: 0.0054 (5) |
| $wR(F^2) = 0.0885$ | Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1) |
| $S = 1.068$ | Absolute configuration: Flack (1983) parameter $\chi = 0.22\,(2)$ |
| 1621 reflections | |
| 265 parameters | |
| H-atom parameters not refined | |
| $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.4177P]$ where $P = (F_o^2 + 2F_c^2)/3$ | |
| $(\Delta/\sigma)_{max} = 0.007$ | |
| $\Delta\rho_{max} = 0.26$ e Å$^{-3}$ | |
| $\Delta\rho_{min} = -0.18$ e Å$^{-3}$ | |

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cl | 0.3453 (2) | 0.08956 (6) | 0.17335 (6) | 0.0811 (4) |
| N1 | 0.3390 (4) | 0.2767 (2) | 0.4374 (2) | 0.071 (1) |
| C2 | 0.2910 (4) | 0.1973 (2) | 0.4020 (2) | 0.054 (1) |
| C3 | 0.4491 (4) | 0.1496 (2) | 0.3734 (2) | 0.056 (1) |
| N4 | 0.5169 (3) | 0.1856 (2) | 0.3039 (2) | 0.0504 (8) |
| C5 | 0.5947 (3) | 0.2582 (2) | 0.3001 (2) | 0.0446 (9) |
| C5a | 0.6099 (4) | 0.3130 (2) | 0.3653 (2) | 0.0451 (9) |
| C6 | 0.7573 (4) | 0.3672 (2) | 0.3644 (2) | 0.052 (1) |
| C7 | 0.7928 (5) | 0.4230 (2) | 0.4204 (2) | 0.058 (1) |
| C8 | 0.6800 (5) | 0.4297 (2) | 0.4825 (2) | 0.055 (1) |
| C8*M* | 0.7178 (7) | 0.4900 (3) | 0.5462 (3) | 0.080 (2) |
| C9 | 0.5354 (4) | 0.3792 (2) | 0.4854 (2) | 0.052 (1) |
| C9a | 0.4936 (4) | 0.3191 (2) | 0.4286 (2) | 0.049 (1) |
| C10 | 0.2208 (7) | 0.3017 (4) | 0.4994 (4) | 0.123 (3) |
| C11 | 0.1518 (4) | 0.2109 (2) | 0.3420 (3) | 0.056 (1) |
| N12 | 0.0832 (3) | 0.1333 (2) | 0.3112 (2) | 0.0525 (9) |
| C13 | −0.0550 (4) | 0.0940 (2) | 0.3429 (2) | 0.049 (1) |
| O14 | −0.1266 (3) | 0.1195 (2) | 0.4008 (2) | 0.075 (1) |
| C15 | −0.1156 (4) | 0.0187 (2) | 0.3022 (2) | 0.050 (1) |
| C16 | −0.2500 (4) | −0.0295 (2) | 0.3261 (3) | 0.066 (1) |
| O17 | −0.2740 (4) | −0.0952 (2) | 0.2779 (2) | 0.0751 (9) |
| C18 | −0.1518 (5) | −0.0875 (2) | 0.2229 (3) | 0.069 (2) |
| C19 | −0.0508 (5) | −0.0195 (2) | 0.2350 (2) | 0.061 (1) |
| C1′ | 0.6683 (4) | 0.2790 (2) | 0.2246 (2) | 0.047 (1) |
| C2′ | 0.7551 (4) | 0.2174 (2) | 0.1835 (2) | 0.056 (1) |
| C3′ | 0.8194 (5) | 0.2336 (2) | 0.1120 (3) | 0.066 (1) |
| C4′ | 0.7968 (5) | 0.3122 (3) | 0.0794 (2) | 0.069 (1) |
| C5′ | 0.7122 (5) | 0.3741 (3) | 0.1199 (3) | 0.067 (1) |
| C6′ | 0.6501 (5) | 0.3585 (2) | 0.1926 (2) | 0.055 (1) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| N1—C2 | 1.460 (5) | C11—N12 | 1.451 (4) |
| N1—C9a | 1.373 (4) | N12—C13 | 1.350 (4) |
| N1—C10 | 1.472 (7) | C13—O14 | 1.226 (5) |
| C2—C3 | 1.516 (5) | C13—C15 | 1.475 (5) |
| C2—C11 | 1.514 (5) | C15—C16 | 1.352 (5) |
| C3—N4 | 1.447 (5) | C15—C19 | 1.419 (5) |
| N4—C5 | 1.306 (4) | C16—O17 | 1.362 (5) |
| C5—C5a | 1.447 (5) | O17—C18 | 1.350 (6) |
| C5—C1′ | 1.479 (5) | C18—C19 | 1.350 (5) |
| C5a—C6 | 1.422 (4) | C1′—C2′ | 1.391 (5) |
| C5a—C9a | 1.428 (5) | C1′—C6′ | 1.397 (5) |
| C6—C7 | 1.356 (5) | C2′—C3′ | 1.373 (6) |
| C7—C8 | 1.395 (5) | C3′—C4′ | 1.392 (6) |
| C8—C8*M* | 1.506 (6) | C4′—C5′ | 1.380 (6) |
| C8—C9 | 1.370 (5) | C5′—C6′ | 1.385 (6) |
| C9—C9a | 1.421 (5) | | |
| C9a—N1—C10 | 118.6 (4) | N1—C9a—C5a | 126.2 (3) |
| C2—N1—C10 | 113.4 (3) | C2—C11—N12 | 113.1 (3) |
| C2—N1—C9a | 126.7 (3) | C11—N12—C13 | 121.8 (3) |
| N1—C2—C11 | 110.5 (3) | N12—C13—C15 | 115.2 (3) |
| N1—C2—C3 | 112.2 (3) | N12—C13—O14 | 122.6 (3) |
| C3—C2—C11 | 113.8 (3) | O14—C13—C15 | 122.2 (3) |
| C2—C3—N4 | 111.4 (3) | C13—C15—C19 | 130.2 (3) |
| C3—N4—C5 | 124.1 (3) | C13—C15—C16 | 123.6 (3) |
| N4—C5—C1′ | 114.8 (3) | C16—C15—C19 | 106.2 (3) |
| N4—C5—C5a | 122.3 (3) | C15—C16—O17 | 110.4 (3) |
| C5a—C5—C1′ | 122.9 (3) | C16—O17—C18 | 106.3 (3) |
| C5—C5a—C9a | 127.5 (3) | O17—C18—C19 | 110.9 (4) |
| C5—C5a—C6 | 115.0 (3) | C15—C19—C18 | 106.2 (4) |
| C6—C5a—C9a | 117.5 (3) | C5—C1′—C6′ | 121.8 (3) |
| C5a—C6—C7 | 123.4 (3) | C5—C1′—C2′ | 119.3 (3) |
| C6—C7—C8 | 119.6 (3) | C2′—C1′—C6′ | 118.8 (3) |
| C7—C8—C9 | 119.0 (3) | C1′—C2′—C3′ | 120.8 (3) |
| C7—C8—C8*M* | 120.8 (4) | C2′—C3′—C4′ | 120.2 (4) |
| C8*M*—C8—C9 | 120.2 (4) | C3′—C4′—C5′ | 119.5 (4) |
| C8—C9—C9a | 123.5 (3) | C4′—C5′—C6′ | 120.6 (4) |
| C5a—C9a—C9 | 117.0 (3) | C1′—C6′—C5′ | 120.0 (3) |
| N1—C9a—C9 | 116.7 (3) | | |
| C2—N1—C9a—C5a | 24.4 (6) | N4—C5—C1′—C2′ | −41.8 (5) |
| C9a—N1—C2—C11 | −109.3 (4) | N4—C5—C5a—C9a | −28.8 (5) |
| C9a—N1—C2—C3 | 18.8 (5) | C5—C5a—C9a—N1 | −3.8 (6) |
| N1—C2—C11—N12 | −172.9 (3) | C2—C11—N12—C13 | 89.3 (4) |
| N1—C2—C3—N4 | −75.7 (4) | C11—N12—C13—O14 | −2.7 (6) |
| C2—C3—N4—C5 | 69.4 (4) | C11—N12—C13—C15 | 176.4 (3) |
| C3—N4—C5—C5a | −4.4 (5) | N12—C13—C15—C19 | 0.5 (6) |

The data were collected with a scan width of 60 steps of 0.02° with extra steps for the $\alpha_1$–$\alpha_2$ dispersion. The variable scan speed ranged from 0.5 to 1.5 s per step. The ratio of total background to scan time was 0.5. The structure was solved by direct methods and refined anisotropically by full-matrix least squares on $F^2$. H atoms were positioned geometrically and allowed to ride on their parent atoms.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*2.1 (McArdle, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Peeters, O. M., Blaton, N. M., Meurisse, R. L. & De Ranter, C. J. (1994*a*) *Acta Cryst.* C**50**, 1350–1352.
Peeters, O. M., Blaton, N. M., Meurisse, R. L. & De Ranter, C. J. (1994*b*) *Acta Cryst.* C**50**, 1352–1354.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Stoe & Cie (1988). *DIF*4. *Diffractometer Control Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*a*). *EMPIR. Empirical Absorption Correction Program.* Version 1.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU*4. *Data Reduction Program.* Version 7.08. Stoe & Cie, Darmstadt, Germany.

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# Pyridoxal Isonicotinoyl Hydrazone (PIH), a Synthetic Ion-Chelating Agent

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## Abstract

Pyridoxal isonicotinoyl hydrazone [3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridinecarboxaldehyde 4-pyridinecarbonylhydrazone, $C_{14}H_{14}N_4O_3$] exhibits a non-planar conformation. Non-H atoms lie almost in two planes, one of the isonicotinoyl ring, the other of the remainder of the molecule, with a dihedral angle of 17.41° between them. The central C=N—N′—C=O chain has an *E* configuration around the C=N double bond of the hydrazone bridge, a *trans* motif of the amide group along —N′—C= and an *S-trans* conformation along